Fluorine In Water And Its Quantitative Determination

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THE DETERMINATION OF FLUORINE IN WATER.

The purpose of this research work was to ascertain the location and the quantity of fluorine in water, and to devise a standard method for its quantitative determination.

The presence of fluorine in water has been a known fact for many years, but the determination of the quantity in each water or in any water, to the best of my knowledge, has never been made.

Professor Whitaker, of the University of Kansas, and formerly of Columbia University, while connected with the latter school made extensive tests in regard to the source of fluorine found in the beer manufactured by a well-known eastern brewery. The question came up in connection with a suit brough by the Pure Food Commission against this brewery, in which they were accused of adding fluorine to their beer. They denied the charge and asked Professor Whitaker to work on the investigatio to discover the real source of their fluorine. After very extended research he traced the source of fluorine down to the water which was used in the manufacture of the beer, and there he was able to get a positive test in all samples. Owing to the case being dropped and other work breaking in on Professor Whitaker, his investigation stopped with the discovery that fluorine was to be found in waters and could be easily distinguished.

His inability to carry the work further, due to the causes previously stated, however, did not lessen his interest in the results which could possibly be attained by a thorough investigation or thesis. Through him, Professor C. C. Young,

of the Water Analysis Department of the University of Kansas, became very much interested in the subject. After considerable thought and exchange of ideas as to the source and quantity of fluorine in the waters of the State of Kansas, Professor Young gave me the opportunity to do work under his supervision for my graduating thesis on the subject of fluorine, its occurrence in waters, and the formation of a standard method for its quantitative determination.

I was pleased and honored by this opportunity of working under Professor Young, and I accepted and have carried out to the best of my ability the work laid out by him.

The method used by me is the same as the one found so effective by Professor Whitaker in his analysis of beer with the addition of a quantitative determination. The proceedure is to make, from a standard solution of a known fluoride, a complete set of standard etchings ranging from 1 part fluorine to 1,000 parts of water, to 1 part in 1,000,000 parts of water. Having these standards made up, waters, collected from various parts of the state, were tested by precipitating any fluorine present with $Ca\ Cl_2$, filtering upon a dry filter, drying residue in a platinum crucible over a flame and then making an etch on white French glass by means of the addition of H_2SO_4 to the precipitate.

The etching thus obtained is then compared with the standards previously prepared, and by means of accurate comparison the exact standard representing the exact amount of fluorine present is chosen and then the water is said to contain the amount of fluorine in parts-per-million which the slide shows.

The apparatus used in making the etchings is very simple and easily handled. It consists of a platinum crucible of 1 inch to $1\frac{1}{2}$ inches in diameter at the top, and having a flat bottom. In this crucible is placed the precipitate from the water to be tested, and H_2SO_4 is added to liberate the HF. gas. On top of this crucible is placed a slide of white French glass, the lower surface of which is covered with a wax of comparatively low melting point. Through the wax the name of the water, or some number, is written on the glass, making it the only glass surface where the HF. gas can attack and give an etch. Above the glass slide is a copper cooler so constructed as to permit the continued passage of cold water through it by means of rubber tubing connection to the tap. This cooler keeps the wax on the slide from melting and eliminating the lettering and thus making an etch impossible. This crucible, slide and cooler rest on an asbestos gauze on a tripod of sufficient height to give room for a Bunsen burner, burning low enough so as not to heat the platinum crucible sufficiently to melt the wax on the slide. The apparatus is very simple.

My proceedure in carrying out this method is as follows:

My first step was to obtain some white French glass of uniform quality and thickness. The best I could do was to purchase from Wolf's Book Store, Lawrence, Kansas, the white French glass used by them for framing pictures. My next preliminary step was to order my copper cooler constructed after the model invented and used by Professor Whitaker in his determinations. This cooler consisted of a cylindrical copper vessel 2 inches high and 3 inches in diameter, closed at both ends. From the

side and near the top, a copper tube one inch long issued perpendicular to that side, and directly opposite and issuing from a point near the bottom was a like tube. This, with rubber tubing, was the cooler complete.

Having prepared my glass and my cooler, I now made arrangements to make up my standard etchings. I thoroughly waxed the inside of all my bottles and pipettes by pouring molten wax into each and allowing it to harden on the sides in a thin layer. This layer afforded the glass a protection from the fluorine, and also afforded the solutions a protection from loss of fluorine.

Having made a thorough covering on each utensil, I then proceeded to make up a solution of NH_4F in water.

$\frac{N}{10}$ NH_4F = 3.7032 grams/liter.

Fluorine in $\frac{N}{10}$ NH_4F = 1.9 grams/liter.

I weighed out sufficient to make 5 liters of $\frac{N}{10}$ NH_4F or 18.516 grams NH_4F.

Fluorine in 18.516 grams NH_4F = 9.5 grams.

Bottle was 4.5 liter capacity. Made solution up to 4 liters giving

$\frac{9.5}{4}$ = 2.37 grams fluorine per liter.

1 cc. of solution = .00237 grams F.

Having now my main standard fluorine solution, I undertook by a series of dilutions to obtain solutions corresponding to those in the following table:

TABLE OF STANDARDS.

Parts of Fluorine	Parts of Water
1	1,000
1	2,000
1	3,000
1	4,000
1	5,000
1	6,000
1	7,000
1	8,000
1	9,000
1	10,000
1	11,000
1	12,000
1	13,000
1	14,000
1	15,000
1	16,000
1	17,000
1	18,000
1	19,000
1	20,000
1	25,000
1	30,000
1	35,000
1	40,000
1	45,000
1	50,000
1	55,000
1	60,000
1	65,000
1	70,000
1	75,000
1	80,000
1	85,000
1	90,000
1	95,000
1	100,000
1	200,000
1	300,000
1	400,000
1	500,000
1	600,000
1	700,000
1	800,000
1	900,000
1	1,000,000.

As each of the above series was completed I at once added $CaCl_2$ to a 100 cc. portion of each solution to precipitate the fluorine as CaF_2. Here I ran up against difficulties.

I evaporated the solution, from which the fluorine had been precipitated, almost to dryness, and transferred the precipitate and solution to the platinum crucible where the evaporation was completed until the precipitate was perfectly dry. This process in itself was extremely long, taking from one to one and one-half hours, and in addition the etching took a half hour, making the time element one of great moment. And besides this, a good part of the precipitate was either lost during the transference from beaker to crucible or during the heating in the crucible due to spurting.

At any rate my results were not accurate and varied considerably; for instance, a solution containing a larger amount of fluorine gave less of an etch than one containing a smaller amount.

I also found out at this time that the height of the Bunsen flame must be regulated accurately to the same height each time in order to give good results. A fraction of a centimeter above this height will superheat the crucible above the temperature needed to decompose and hasten the HF. reaction, and the surplus heat will go to melt the wax on the slide. A lower flame will make action slower, and so in order to have uniform standard conditions the flame must always be the same exact height, and the distance from burner to gauze must be constant.

I obtained the best results from a $2\frac{1}{2}$ cm. flame, and the gauze $14\frac{1}{2}$ cm. above the top of the burner. These are my standard conditions for all the results which follow. I also found that a mixture of 1/2 paraffin and 1/2 Kanachba wax gave the best workable high melting point wax to be used to cover slides with.

To save the time element, and the loss of fluorine, I tried precipitating the fluorine as CaF_2 as before, and in addition adding a few drops of a solution of Na_3PO_4 to precipitate some of the $CaCl_2$ as $Ca_3(PO_4)_2$ to add body to the original residue, and so make it more easily handled. This precipitated $Ca_3(PO_4)_2$ when mixed with the solution and allowed to settle carried down with it all suspended particles of CaF_2 in the solution.

This residue was then filtered on to a dry filter paper, which was then transferred to the crucible and all moisture driven off. This method proved very satisfactory. I was now ready to etch.

Here I had another obstacle. I had to determine what strength H_2SO_4 was necessary to give a good etch. This problem I investigated for two days until I at last discovered that the concentrated H_2SO_4 was the only strength which would give results.

So, now I had the best means of handling my precipitate without loss, and also the best means of extracting the HF. from the precipitate, and the best combination of wax for coating the glass, a good cooler, and standard conditions of height of flame and gauze. All that remained now was to make etchings.

To mark my slides I used a glass rod drawn down to a point and the point melted back into a perfectly smooth round ball on the end. This I used for several weeks before I discovered my mistake. I had completed my series of standards, and had commenced to determine the fluorine quantitatively in some samples of waters, when I discovered that I could obtain an etch from any and all of the waters and even from double distilled water, but they differed from a distinct etch to one which could be seen only with great effort and only then by blowing one's breath upon the place where the etch was supposed to be.

There were a few of this latter type, and they caused me to regard my marker with suspicion and to make tests with it. I found that in almost every case where the etch was extremely hard to see, the same water reprecipitated and treated to etch a slide marked with a soft wooden marker did not give the slightest appearance of an etch. From this and from information from Professor Young, I found out that when glass is marked with glass, the appearance of an etch is seen when the breath is blown upon the slide.

This new element made it necessary for me to star all over again and prepare new standards. But, one thing I did learn was that standard etchings below 1 part in 40,000 parts of water were not necessary, as none of the waters contained sufficient fluorine to give a larger test.

Having now everything on a working basis, I again prepared my standard slides, using 100 cc. of solution for each standard, and running each exactly 30 minutes.

I made up the following standards:

STANDARD ETCHINGS

Parts of Fluorine	Parts of Water
1	40,000
1	50,000
1	55,000
1	60,000
1	65,000
1	70,000
1	75,000
1	80,000
1	85,000
1	90,000
1	95,000
1	100,000
1	200,000
1	300,000
1	400,000
1	500,000
1	600,000
1	700,000
1	800,000
1	900,000
1	1,000,000.

These standards were exact and were perfectly made.

The next discovery that I made was that if some of the waters where I used 100 cc. samples, and ran them 30 minutes, were run one hour, I obtained an etch where before the plate was clear. This lead me to make a series of tests to see if a regular difference in time would make a perfectly regular difference in etch, or in other words twice the time twice the etch.

I spent three days making tests of ten samples of the same solution, run 30 min., 1 hr., 1½ hrs., 2 hrs., 2½ hrs., 3 hrs., 3½ hrs., 4 hrs., 4½ hrs., and 5 hrs., respectively, and the results were as I expected, and were dependent upon the time and twice the time made twice the etch.

This helped me greatly to obtain results of extreme smallness in quantity and of good quality. For instance, by taking 2,000 cc. of the solution, thus getting 20 times the amount of precipitate that would be in 100 cc., and etching 2 hours or 4 times the time for the standard etchings, the etch as appeared would be 20x4 = 80 times as great as that for 100 cc. and 30 minutes. Extremely small quantities of fluorine could be found and a quantitative determination made.

Now everything was ready to test the waters over the state, my standards were prefected, and my apparatus and methods were exact.

My first step was to test Lawrence, Kansas, waters, and as the city tap water was right at my sink I made an investigation of it. The Lawrence City Water Works Company obtain their water from deep wells near the bank of the Kaw River, and yet as far back as the source of these wells can be traced they are in no place in connection with the river. I ran the following tests upon this water:

LAWRENCE CITY TAP WATER

Sample Tested	Time Tested	Etch
100 cc.	30 min.	none
500 cc.	30 min.	none
500 cc.	1 hour	none
2,500 cc.	3½ hours	none.

This was sufficient evidence to me that fluorine was not present in the Lawrence City Tap., for if I had obtained an etch which corresponded with my standard 1 pt. F. to 1,000,000 H_2O, then the amount of fluorine would not be worth figuring for, since

Standard 1-1,000,000 = 30 min. and 100 cc.

Etch = 7x30 mm. and 25x100 cc.

100 cc. Tap water run 30 min. = $\frac{1}{175} \times \frac{1}{1,000,000}$

The smallest result possible = .0057 pts. F. - 1,000,000 H_2O.

KAW RIVER WATERS

	Sample Tested	Time Tested	Etch
(1)	1,000 cc.	1 hr.	yes
(2)	2,000 cc.	2 hrs.	yes.

Standard for (1) = 1 F. - 100,000 H_2O.

Standard for (2) = 1 F. - 20,000 H_2O.

100 cc. (1) = $\frac{1}{10} \times \frac{1}{2} \times \frac{1}{100,000}$ = .5 pts./1,000,000.

100 cc. (2) = $\frac{1}{20} \times \frac{1}{4} \times \frac{1}{25,000}$ = .5 pts./1,000,000.

LAWRENCE WELL WATERS

504 Ohio St., one block south from the river bank:

Sample Tested	Time Tested	Etch
1,000 cc.	2 hrs.	none
2,000 cc.	4 hrs.	none.

512 Ohio St., near river:

Sample Tested	Time Tested	Etch
1,500 cc.	2 hrs.	none
1,000 cc.	2 hrs.	none
1,000 cc.	4 hrs.	none.

441 Ohio St., 200 feet from Kaw River:

Sample Tested	Time Tested	Etch
2,000 cc.	2 hrs.	none
1,000 cc.	3 hrs.	none.

1346 Tennessee St., at foot of hill:

Sample Tested	Time Tested	Etch
1,000 cc.	3 hrs.	none
2,000 cc.	4 hrs.	yes.

Standard = 1 pt. Fluorine/ 400,000 H_2O, reduced to stand. cond. of 100 cc. and 30 min.

Fluorine in the water = $\frac{1}{20} \times \frac{1}{8} \times \frac{1}{400,000}$

= 1 - 64,000,000

= .0156 pts. fluorine/1,000,000 pts. H_2O.

1624 Tennessee St., at foot of hill:

Sample Tested	Time Tested	Etch
2,000 cc.	2 hrs.	yes
(2) 2,000 cc. (dropped (2)).	2 hrs.	yes.

Standard = 1 - 75,000.

100 cc. = $\frac{1}{20} \times \frac{1}{75,000} = \frac{1}{1,500,000}$

30 m = $\frac{1}{20} \times \frac{1}{1,500,000} = \frac{1}{6,000,000}$, standard condition of 100 cc. and 30 min.

Fluorine present = .1666 pts. F./ 1,000,000 pts. H_2O.

1423 Kentucky St., 500 feet from foot of hill:

Sample Tested	Time Tested	Etch
1,000 cc.	2 hrs.	none
2,000 cc.	3 hrs.	none.

1646 Kentucky St.:

Sample Tested	Time Tested	Etch
1,500 cc.	2 hrs.	none
1,500 cc.	4 hrs.	none.

From the above results obtained by testing representative waters in the City of Lawrence, the wells free from drainage from the river or other surface waters showed the absence of fluorine, while the river and the wells situated at the foot of Mt. Oread gave good positive tests which tend to show the presence of fluorine in surface waters.

I then made a series of tests on waters taken at random from the cities and towns in Kansas, and the following results were obtained:

#4868, TOPEKA, KANSAS.

Water from well sent to Water Analysis Department for complete analysis by Otto Kuehne Company.

Sample Tested	Time Tested	Etch
1,000 cc.	2 hrs.	yes.

Standard 1 - 200,000.

100 cc. $= \frac{1}{10} \times \frac{1}{200,000} = \frac{1}{2,000,000}$.

30 m. $= \frac{1}{4} \times \frac{1}{2,000,000} = \frac{1}{8,000,000}$.

Standard condition of 100 cc. and 30 m.

Fluorine present = .125 pts./1,000,000 pts. H_2O.

#4857, BLUE RAPIDS, KANSAS.

Water sent by Roy Henry of the Ann. Cement & Plaster Co.

Sample Tested	Time Tested	Etch
1,000 cc.	2 hrs.	none.

#4884, LEAVENWORTH, KANSAS.

Water from a spring, suspected of surface drainage, sent by Dr. H. J. Stacey.

Sample Tested	Time Tested	Etch
1,000 cc.	1 hr.	yes.

Standard 1 - 400,000.

100 cc. = 1 - 4,000,000.

30 min. $= \frac{1}{2} \times \frac{1}{4,000,000} = \frac{1}{8,000,000}$, standard condition of 100 cc. and 30 min.

Fluorine present = .125 pts./1,000,000 H_2O.

#4866, MERRIAM, KANSAS.

Water from Blue Jacket Spring sent in by W. C. Bain.

Sample Tested	Time Tested	Etch
1,000 cc.	2 hrs.	yes.

Standard = 1 - 400,000

100 cc. = $\frac{1}{10} \times \frac{1}{400,000} = \frac{1}{4,000,000}$.

30 min. = $\frac{1}{4} \times \frac{1}{4,000,000} = \frac{1}{16,000,000}$.

Standard condition 100 cc. and 30 min.

Fluorine present = .0625 pts./1,000,000 pts. H_2O.

#4879, BURR OAK, KANSAS.

Water from proposed water supply sent in by J. E. Hawley.

Sample Tested	Time Tested	Etch
900 cc.	2 hrs.	yes.

Standard = 1 - 100,000.

100 cc. = $\frac{1}{9} \times \frac{\quad}{100,000} = \frac{1}{900,000}$.

30 min. = $\frac{1}{4} \times \frac{\quad}{900,000} = \frac{1}{3,600,000}$.

Standard condition of 100 cc. and 30 min.

Fluorine present = .278 pts./1,000,000 H_2O.

#4883, QUINTER, KANSAS.

Water sent in by Dr. Stover.

Sample Tested	Time Tested	Etch
1,000 cc.	30 min.	yes.

Standard = 1 - 500,000.

100 cc. = $\frac{1}{10} \times \frac{1}{500,000} = \frac{1}{5,000,000}$.

Standard condition 100 cc. and 30 min.

Fluorine present = .2 pt./1,000,000 pts. H_2O.

#4878, BURR OAK, KANSAS.

Sample sent in by Dr. J. E. Hawley.

Sample Tested	Time Tested	Etch
1,000 cc.	2 hrs.	none.

This water was for proposed city water supply.

#4872, TOPEKA CITY WATER WORKS.

Sample Tested	Time Tested	Etch
1,000 cc.	2 hrs.	none.

All this time I had had a desire to analyze some good brand of beer and ascertain the exact amount of fluorine present. I obtained several samples of Budweiser beer and made tests.

BUDWEISER BEER

	Sample Tested	Time Tested	Etch
(1)	500 cc.	30 min.	none
(2)	500 cc.	1 hour	yes
(3)	1,000 cc.	2 hours	yes.

Number (1) dumped over.

(2) Standard = 1 - 200,000.

$$100 \text{ cc.} = \frac{1}{5} \times \frac{1}{200,000} = \frac{1}{1,000,000}.$$

$$30 \text{ min.} = \frac{1}{2} = \frac{1}{2} \times \frac{1}{1,000,000}.$$

Standard condition 100 cc. and 30 min.

Fluorine present = .5 part/1,000,000 pts. H_2O.

(3) Standard = 1 - 50,000.

$$100 \text{ cc.} = \frac{1}{10} \times \frac{1}{50,000} = \frac{1}{500,000}.$$

$$30 \text{ m.} = \frac{1}{4} \times \frac{1}{500,000} = \frac{1}{2,000,000}.$$

Standard condition of 100 cc. and 30 min.

Fluorine present = .5 part/1,000,000 pts. H_2O.

I also made several tests with bottled water from the Condal Spring, Spain.

RUBINAT - CONDAL SPRING, SPAIN.

Sample Tested	Time Tested	Etch
1,000 cc.	30 min.	none
500 cc.	30 min.	none
1,000 cc.	3 hrs.	yes.

Standard = 1 - 50,000.

100 cc. $= \frac{1}{10} \times \frac{1}{50,000} = \frac{1}{500,000}$.

30 m. $= \frac{1}{6} \times \frac{1}{500,000} = \frac{1}{3,000,000}$.

Standard condition of 100 cc. and 30 min.

Fluorine present = .333 pts./1,000,000 parts H_2O.

If you will now glance carefully over the results in all my tests, you will find as I did that the waters divide themselves into two main groups: (1) Those containing fluorine; and (2) those not containing fluorine. And when I looked again at group (1) and studied it carefully, I was surprised to discover that it contained surface waters, river waters, wells at the foot of the Hill in Lawrence, samples of spring water suspected of pollution, and samples of well waters sent in by the health officers to be examined for pollution, and, last, mineral waters and beer. While in (2) I found waters from good wells not subject to drainage, although some of them very near the river with its high percentage of fluorine, and even the city waters of Lawrence and Topeka whose wells are close to the river's edge.

I thought over this subject for a few days and came to this conclusion. The pollution of the wells and rivers must cause the presence of fluorine, and that the fluorine as fluorides must be dissolved or suspended in surface waters which find their way into the wells and rivers. This was logical, but where was the fluorine to come from?

I at once consulted Professor Haworth, of the Mining & Geology Department, and asked him concerning the occurrence of fluorine as fluoride in the vicinity of Lawrence and covering the whole state. He said that Fluorspar and Apatite contain considerable fluorine, but that the former was very rarely found in Kansas. The latter, however, was found in almost all soils in varying quantities. He also said that from tests of thirty samples of Apatite gathered from different parts of the State of Kansas, twenty-two gave tests of fluorine.

Since apatite was a common constituent of all soils, why wouldn't the rains and surface waters leach it out and hold it in suspension? This was one source of fluorine which could be tested.

I obtained some samples of Fluorspar and Apatite, ground them up very fine, and placed each in a separatory funnel having an asbestos plug for filter. I then prepared four liters of water containing CO_2 and standardized it with $\frac{N}{50} Na_2CA_3$ and found that it contained 252.56 parts CO_2 per one million parts of water. I then poured this CO_2 water into the funnels containing Fluorspar and Apatite and allowed it to filter down through the ground rock.

I then treated the filtrates in the same manner as I had the original waters containing fluorine, by adding $Ca\ Cl_2$ and Na_3PO_4 allowing it to stand and filter. I then made etchings from each.

FLUORSPAR

Sample Tested	Time Tested	Etch
1,000 cc.	2 hrs.	yes.

Standard = 1 - 75,000.

100 cc. = 1 - 750,000.

30 m. = $\frac{1}{4}$ x $\frac{1}{750,000}$ = 1 - 3,000,000.

Standard condition of 100 cc. and 30 min.

Fluorine = .333 pts./1,000,000 H_2O.

APATITE

Sample Tested	Time Tested	Etch
600 cc.	3 hrs.	yes.

Standard = 1 - 100,000.

Standard conditions of 100 cc. and 30 min.

Fluorine present = $\frac{1}{6}$ x $\frac{1}{6}$ x $\frac{1}{100,000}$ = $\frac{1}{3,600,000}$,

= .277 pts./1,000,000 pts. H_2O.

This was sufficient proof to me that there was a possibility of rains and surface waters leaching fluorine out of Fluorspar and Apatite and finding their way into wells and rivers.

Professor Henry P. Talbot, of the Massachusetts Institute of Technology, in some of his research work discovered that malt and grain contained a small amount of fluoride, and that the glaze and outer covering of most plants was made of fluorine as fluoride. He attributed the cause of fluorine in beer to the malt, and did not consider the water. The Budweiser Company in St. Louis use the Mississippi River water, which, like the Kaw River, probably contains about .5 part fluorine/million parts H_2O.

This glaze on plants and grain gives another source of fluorine, and the rains may leach it out and join it to that from the Apatite.

In future years pollution of wells by surface waters may be tested by making a fluorine analysis, and also the extent of pollution measure.

This work is by no means finished, and further work may lead to new discoveries.